



Enthalpy of formation and disordering temperature of transient monotropic liquid crystals of poly(butylene 2,6-naphthalate)

René Androsch^{a,*}, Michelina Soccio^b, Nadia Lotti^b, Dieter Jehnichen^c, Michael Göbel^c, Christoph Schick^{d,e}

^a Interdisciplinary Center for Transfer-oriented Research in Natural Sciences (IWE TFN), Martin Luther University Halle-Wittenberg, 06099 Halle/Saale, Germany

^b Civil, Chemical, Environmental and Materials Engineering Department, University of Bologna, Via Terracini 28, 40131, Bologna, Italy

^c Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden, Germany

^d University of Rostock, Institute of Physics and Competence Center CALOR, Albert-Einstein-Str. 23–24, 18059 Rostock, Germany

^e Kazan Federal University, 18 Kremlyovskaya Street, Kazan 420008, Russian Federation

HIGHLIGHTS

- Crystallization of PBN below 160 °C follows Ostwald's rule of stages.
- Crystallization below 160 °C proceeds via formation of a liquid crystalline (LC) phase.
- Disorder of the LC-phase was analyzed on fast heating, suppressing the transition into crystals.
- Disorder of the LC-phase occurs 20–30 K lower than melting of α -crystals.
- The bulk enthalpy of LC-phase formation is about 20–25 % of that of crystallization.

ARTICLE INFO

Keywords:

Poly(butylene 2,6-naphthalate)

Liquid crystal

Crystallization

Fast scanning chip calorimetry

ABSTRACT

Melt-crystallization of poly(butylene 2,6-naphthalate) (PBN) at temperatures lower than about 160 °C follows Ostwald's rule of stages via intermediate formation of a smectic liquid crystalline phase (LC-phase). The transient LC-phase has been isolated by interruption of the isothermal crystallization process at 140 °C at sub-second timescale, and then its disordering was analyzed on heating at a rate of 2000 K/s, which suppresses the transition into α -crystals. The disordering temperature of the LC-mesophase is slightly lower than 200 °C, and as such 20–30 K lower than the melting temperature of α -crystals formed from the LC-phase at 140 °C. Analysis of the bulk enthalpy of formation of the LC-phase revealed that it covers only 20–25% of the total bulk enthalpy of crystallization, which is considered further proof of its smectic nature.

1. Introduction

Poly(butylene 2,6-naphthalate) (PBN) is a linear crystallizable polyester forming different crystal polymorphs as a function of the crystallization conditions. Crystallization on slow cooling of the melt at rates lower than about 10 K/min (0.167 K/s), or at temperatures higher than about 200 °C causes formation of triclinic β' -crystals [1–3] with an equilibrium melting temperature of 281 °C [4]. The β' -crystals form dendritic spherulites, which is attributed to their rather individual growth in direction parallel to the spherulite radius [3]. If the cooling rate is between 10 and 0.1 K/min (0.167 and 0.017 K/s), or if the crystallization temperature is lower than 230 °C, then β' -crystals are increasingly replaced by triclinic α -crystals; crystallization below about

200 °C yields α -crystals only. Related to the lower packing density compared to the β' -phase, the equilibrium melting temperature of the α -phase of 261 °C is about 20 K lower than that of β' -crystals [4]. While in the β' -phase the flexible butylene units adopt a nearly all-*trans* chain conformation, in case of α -crystals the fiber identity period (FIP) is shortened [5–7]. Growth of α -crystals occurs spherulitically with the typical appearance of a distinct Maltese cross when observed by polarized-light optical microscopy (POM) [3].

Formation of both β' - and α -crystals, at temperatures higher than about 160 °C, occurs directly from the melt. However, if the melt is supercooled to temperatures lower than about 160 °C, by cooling faster than a critical rate of the order of magnitude of 10^0 – 10^1 K/s [8], then crystallization proceeds via intermediate formation of a liquid

* Corresponding author.

E-mail address: rene.androsch@iw.uni-halle.de (R. Androsch).

<https://doi.org/10.1016/j.polymer.2018.10.037>

Received 28 August 2018; Received in revised form 2 October 2018; Accepted 16 October 2018

Available online 23 October 2018

0032-3861/ © 2018 Elsevier Ltd. All rights reserved.